Appl Petrochem Res (2016) 6:361–366
DOI 10.1007/s13203-016-0148-z

ORIGINAL ARTICLE

Adsorption desulfurization study with ionic liquid compound ZrO_2/PSMIMHSO$_4$

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Received: 13 November 2014 / Accepted: 29 January 2016 / Published online: 23 February 2016

Abstract Two ionic liquids 1-methyl-imidazolium-3-propylsulfonate (PSMIM) and 1-methyl-imidazolium-3-propylsulfonate hydrosulfate (PSMIMHSO$_4$) were synthesized. Their ZrO_2, $ZrOCl_2$ and ZrO_2/SO_4^{2-} derivatives were prepared under different condition and their desulfurization performances were studied. Then compared with traditional materials and their original materials under the same condition, the result showed that PSMIMHSO$_4$ compounded with ZrO_2 at mass ratio of 1:1 exhibited the superior desulfurization activity at 433 K for 25 min with the material/oil (m/v) of 1:10, and its desulfurization rate reached 97.4 %.

Keywords Ionic liquid · Desulfurization · Adsorption

Introduction

In recent years, large amounts of fuel oils have been demanded in industries and daily life with the rapid development of society. At the same time, environmental concerns have also attracted more attention [1–3]. That can be attributed to the main exhaust gas SO_x, a major source of acid rain, and poison noble metal catalysts that are irreversibly generated by automobiles. Consequently, desulfurization is highly recommended and restricted in oil and automotive industries in the developed countries, and being research focus in both industry and academia. Presently, desulfurization is mainly carried out by catalytic hydrodesulfurization at the industry. This method can effectively remove aliphatic and alicyclic sulfur compounds from gasoline and diesel [4, 5], but it is difficult to completely remove thiophene and its derivatives. On the other hand, hydrodesulfurization technology need high cost of equipment and operation as well as other drawbacks [6].

Ionic liquids (ILs) have negligible vapor pressure; therefore, they cannot emit volatile organic compounds (VOCs) to the environment. Due to their salt-like characteristics, they are nonvolatile, are nonflammable, and possess high ionic conductivity. ILs are also a highly solvating and non-coordinating medium. ILs consisting of a cation and anion combination are limitless in number. Their physiochemical properties can be determined by both the cations and anions of the salt. ILs have been recently recognized as environmentally benign alternative solvents due to its advantages in minimizing solvent consumption, guaranteeing catalyst performance, and solving various organic/inorganic compounds, which facilitate the reaction efficiency in homogeneous phase, liquid–liquid separation, and IL solvent–catalyst recycling. In addition, this method can be conducted under moderate reaction conditions and easy to recycle the materials. The method combining the chemical oxidation with ionic liquids extraction was the remarkable advantage of this process over the desulfurization by mere solvent extraction with IL, and it could achieve deep desulfurization [7–11].

In this article, we synthesized 1-methyl-imidazolium-3-propylsulfonate (PSMIM) and 1-methyl-imidazolium-3-propylsulfonate hydrosulfate (PSMIMHSO$_4$) and their derivatives by adding ZrO_2, $ZrOCl_2$ and ZrO_2/SO_4^{2-} as adsorbents, and characterized them. Then we studied the optimum temperature and mass ratio of compound materials, and characterize their desulfurization activity under

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same condition in the desulfurization reaction by gas chromatography.

Experimental

Preparation of PSMIM and $PSMIMHSO_4$

1,3-Propanesultone (40.0 g) was completely dissolved in 300 mL toluene. *N*-methyl imidazole (27.0 g) was slowly added with stirring under ice bath. The temperature was slowly raised to 298 K and maintained for 2 h. The product was then filtered from the mixture liquid and washed with diethyl ether and ether acetate three times, respectively. Then it was obtained after 5 h of heating at 373 K [12]. PSMIM (23.3 g) was dissolved in 100 mL of deionized water. Then sulfuric acid (10.9 g) was slowly added with stirring at room temperature. After that, the temperature was raised to 363 K and then maintained for 2 h. Deionized water was removed from the product with rotary evaporator [12].

Preparation of ZrO_2 and ZrO_2/SO_4^{2-}

Zirconium salt solution was prepared by dissolving $ZrOCl_2{\cdot}8H_2O$ (32.2 g) in 800 mL deionized water, 200 mL ammonia solution was then added under vigorous stirring to prepare the sediment of $Zr(OH)_4$. After 2 h, the pH value of the solution was adjusted to 10.3 and stabilized for another 12 h. $Zr(OH)_4$ was filtered from the solution and washed with deionized water to remove Cl^- [13, 14]. ZrO_2 was grinded into powder with the size smaller than 100 mesh, then added into 100 mL 0.1 mol/L·H_2SO_4 solution. After 24 h, the solid was filtered and dried at 373 K for 2 h. After drying, the sample was calcined at 893 K for 6 h [14].

Preparation of compound systems

$PSMIMHSO_4$ was mixed with $ZrOCl_2{\cdot}8H_2O$ named PSC at the mass ratio of 1:1 at 433 K for 2 h, $PSMIMHSO_4$ was mixed with ZrO_2 named PSO and ZrO_2/SO_4^{2-} named PSS under same condition.

Characterization and evaluation of the catalyst

Infrared spectrometer (AVATAR 370 from Thermo Nicolet) was used to analyze at 500–4000 cm^{-1}.

X-ray diffractometer (Deutschland RUKER D2 PHASER) was scanned with CuKα in the range of 10°–80° at a rate of 0.02 s^{-1}.

PSMIM ^{1}HNMR(400 MHz, D_2O): δ2.138(m, 2H, $J = 7.2$ Hz), 2.822(t, 2H, $J = 7.2$ Hz), 3.806(s, 3H), 4.270(t, 2H, $J = 7.2$ Hz), 7.365(s, 1H), 7.437(s, 1H), 8.655(s, 1H). ^{13}CNMR(400 MHz, D_2O): δ25.11, 35.73, 47.24, 47.72, 122.16, 123.76, 136.17.

$PSMIMHSO_4^1$HNMR(400 MHz, D_2O): δ2.135(t, 2H, $J = 7.2$ Hz), 2.745(s, 2H), 3.717(s, 3H), 4.181(t, 2H, $J = 7.2$ Hz), 7.271(s, 1H), 7.339(s, 1H), 8.560(s, 1H). ^{13}CNMR(400 MHz, D_2O): δ24.99, 35.65, 47.15, 47.65, 122.10, 123.71, 136.06.

Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer for C, H, N and S. Anal. calc. for PSMIM: C, 41.18 %; H, 5.88 %; N, 13.73 %; S, 15.69 %; found: 41.24 %; H, 5.83 %; N, 13.74 %, S, 15.65 %. Anal. calc. for $PSMIMHSO_4$: C, 27.81 %; H, 4.64 %; N, 9.27 %; S, 21.19 %; found: C, 27.83 %; H, 4.60 %; N, 9.33 %; S, 21.14 %.

Compound ILs was washed with deionized water and removed from the test tube. The un-reacted $PSMIMHSO_4$ was filtered. The solid was dried at 373 K, and then put into the tube furnace at temperature of 393 K under the protection of N_2, to adsorb pyridine vapor for 30 min.

Desulfurization

Benzothiophene (BT, 5.0 g) was completely dissolved into n-heptane to prepare 5000 ppm model oils. Material (0.5 g) and 5 mL of 5000 ppm benzothiophene (BT) solution were added into a tube. The tube was located in the water bath kettle at the desired temperature and stirred with the speed of 10,000 r/min. Then subnatant was injected into gas chromatography to check the sulfur residue in the solute. The conditions of gas chromatography: keeping the initial temperature at 403 K for 2 min, then raising the temperature to 533 K at the rate of 10 K/min and then maintaining 8 min. The injection volume of the sample is 5 μL.

Desulfurization efficiency is obtained using the internal standard method. The calculation formula is:

$$W = \frac{C_0 - C_X}{C_0} \times 100\,\% \quad (1)$$

where W is desulfurization rate, C_0 is the initial sulfur content of the oil, C_x is the sulfur content of the oil after desulfurization.

Result and discussion

Characterization

Figure 1 shows the FT-IR spectra of ionic liquids. The peaks at 3156, 3116 and 1575 cm^{-1} represent –N–H –C–H and –C=N– stretching vibration of the imidazole ring, respectively. The C–H stretching vibration of CH_2 was observed at 2965 cm^{-1}, the bands at 1487 and 1398 cm^{-1}

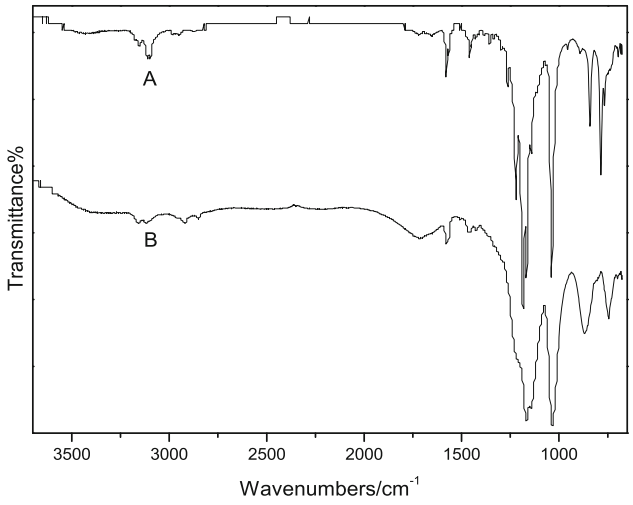

Fig. 1 FT-IR of ionic liquids *A*: PSMIM and *B*: $PSMIMHSO_4$

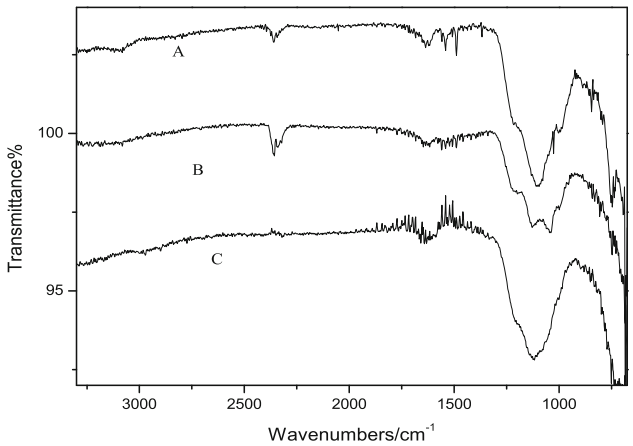

Fig. 2 FT-IR of solid acid prepared under different conditions *A*: ZrO_2/SO_4^{2-} adsorb pyridine, *B*: PSO adsorb pyridine and *C*: ZrO_2/SO_4^{2-}

are formation vibration of $N–CH_2$ and $N–CH_3$. The peak at 749 cm^{-1} is the bending vibration of the imidazole ring. Meanwhile, the bands at 1170 and 1130 cm^{-1} are assigned to the S=O asymmetric and symmetric stretching vibrations of the $–SO_3H$ group for the five kinds of ionic liquids [12].

Figure 2 is FT-IR of solid acid prepared under different conditions. $ZrOCl_2·8H_2O$ is completely dissolved into $PSMIMHSO_4$ at 433 K. So the characteristic peaks of $ZrOCl_2·8H_2O$ do not show up. The peak at 750 cm^{-1} is the Zr–O–Zr or O–Zr–O vibration of ZrO_2/SO_4^{2-}. At the same times, the peak from 1130 cm^{-1} is S=O vibration of ZrO_2/SO_4^{2-}. The peaks at 1450 and 1540 cm^{-1} are characteristic peak of pyridine to check the acid sites. Meanwhile the peaks at 1300 and 1550 cm^{-1} represent –C=C and C=N– stretching vibration of pyridine. On the other hand, the peak at 1625 cm^{-1} is O–H formation vibration and 3400 cm^{-1} is O–H stretching vibration [14, 15].

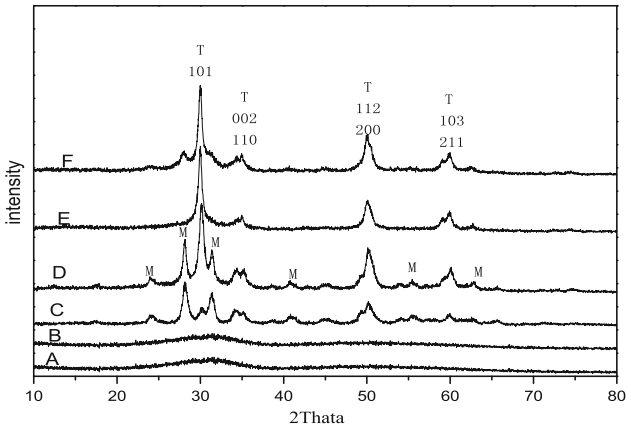

Fig. 3 XRD of under different conditions of preparing solid acid (*T* tetragonal, *M* monoclinic) *A*: ZrO_2–433 K, *B*: PSO, *C*: ZrO_2–893 K, *D*: ZrO_2/SO_4^{2-} 893 K, *E*: PSO calcined at 893 K and *F*: PSO calcined at 893 K after desulfurization

XRD patterns of the solid acids under different conditions are shown in Fig. 3. XRD patterns of all solid acids at 30°, 35°, 50° and 60° are the characteristic feature of tetragonal zirconia. In addition, the XRD result shows the presence of a monoclinic zirconia phase along with major tetragonal zirconia. The hump at 28° in the fuel-lean sample is characteristic of the monoclinic phase. The calcined ZrO_2 at 433 K appears a very broad peak from A and B. The calcined ZrO_2 at 893 K appears the characteristic peak from C. Compared with C, the amount of tetragonal phase is gradually increasing in the D and E, especially in the E which has weak monoclinic peaks [13–17].

The effect of different mass ratio at different temperatures

The effect of reaction temperature on compound ionic liquids is listed in Table 1. The results show that the desulfurization rate of compound ionic liquids increases with the increase of the reaction temperature range from 313 to 353 K and thereafter remained nearly constant, indicating a nearly equilibrium desulfurization rate. The optimum reaction temperature is found to be 353 K.

The effect of $PSMIMHSO_4/ZrO_2$ mass ratios on the desulfurization rate is listed in Table 1. The mass ratio of $PSMIMHSO_4/ZrO_2$ is 1:1, the desulfurization rate increases slightly. The main reason is that the ratio of HSO_4^- increased with $PSMIMHSO_4$, ZrO_2 is easy to compound with HSO_4^-. So the adsorbing activity improves with the desulfurization rate increasing. At the same time, when the mass of ZrO_2 decrease, the adsorbing activity also decline. Therefore, the optimum $PSMIMHSO_4/ZrO_2$ mass ratio is 1:1.

Table 1 Effect of different mass ratio at different temperatures

Temperature (K)	2:1 (%)[a]	1:1 (%)[a]	1:2 (%)[a]	1:3[a] (%)
313	33.9	47.1	38.9	31.3
323	60.1	70.3	65.1	56.5
333	78.2	88.8	81.4	73.7
343	83.9	94.6	87.1	80.6
353	86.4	97.4	90.4	83.1
363	86.6	97.5	90.1	83.5
373	86.2	97.2	90.2	83.3

Condition: the time is 25 min, the amount of PSO is 0.5 g

[a] The mass ratio of $PSMIMHSO_4/ZrO_2$(m/m)

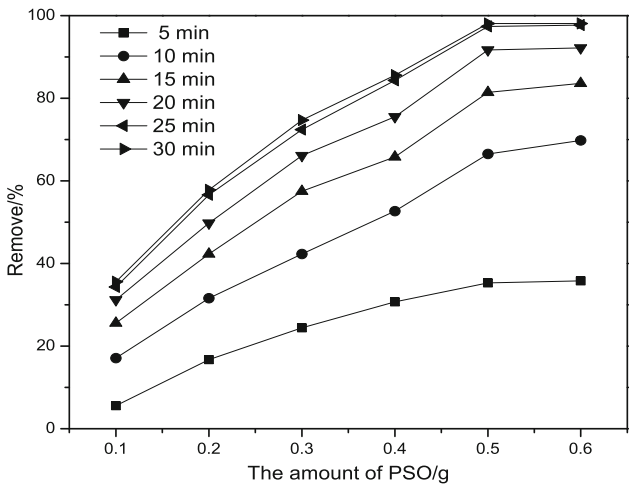

Fig. 4 The effect of the amount of PSO and time condition: the mass ratio of $PSMIMHSO_4/ZrO_2$(m/m) is 1:1, the temperature is 353 K

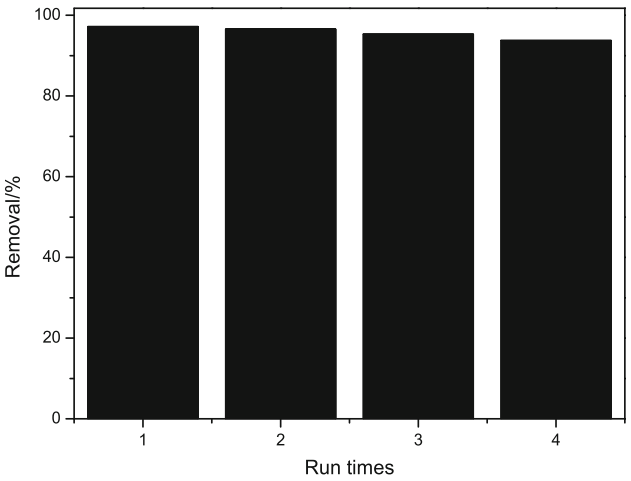

Fig. 5 Recycled activity of PSO

The effect of the amount of PSO and time

The amount of PSO had a great influence on adsorption of BT. When the amount of PSO increased from 0.1 to 0.5 g, the sulfur removal increased remarkably from 34.3 to 97.4 %, but slowly from 97.4 % in 0.5 g to 98.1 % in 0.6 g. The result indicated that the amount of PSO had a significant effect on removal of BT in the desulfurization reaction. To evaluate the role of the time on the reaction efficiency, the adsorption of BT was performed in adsorption desulfurization of BT system. Sulfur removal increased rapidly at the initial stage, but slowly from 97.4 % in 25 min to 98.1 % in 30 min. Thus, it was suitable to carry out the desulfurization reaction with 0.5 g in 25 min (Fig. 4).

The recycled activity of PSO

The property of the PSO is the reusability. The activities of recycled adsorbent are investigated carefully (Fig. 5). The PSO has high stability, and the recycled adsorbing activities are still very high. The rate of desulfurization is still 93.8 % after the PIL has been recycled for 4 times.

Desulfurization rate of different materials

For the ionic liquid PSMIM and the sulfonic acid group functionalized ionic liquid $PSMIMHSO_4$, the acid sites interact well with benzothiophene. At the same time, benzothiophene could be extracted by ionic liquid.

ZrO_2/SO_4^{2-}, ZrO_2 and $ZrOCl_2{\cdot}8H_2O$ all have higher desulfurization ability from Table 2. ZrO_2 is not only BrÖnsted acid, but also Lewis acid, which could coordinate with S element of benzothiophene [18]. The surface of ZrO_2/SO_4^{2-} also has both the acidity of BrÖnsted acid [19] and Lewis acid [20], so ZrO_2/SO_4^{2-} could adsorb benzothiophene. But, due to the influence of Lewis acid site adsorbing water, the rates of desulfurization of ZrO_2/SO_4^{2-}, ZrO_2 and $ZrOCl_2{\cdot}8H_2O$ are weaker than PSO.

The desulfurization rate of PSS is significantly improved in comparison with SO_4^{2-}/ZrO_2, due to the temperature

Table 2 Desulfurization rate of different materials at 353 K for 25 min

The sample number	Component	Desulfurization rate (%)
1	PSMIM	86.3
2	$PSMIMHSO_4$	90.6
3	ZrO_2	90.2
4	ZrO_2/SO_4^{2-}	87.3
5	$ZrOCl_2{\cdot}8H_2O$	92.2
6	PSO	97.4
7	PSS	93.5
8	PSC	90.1

increasing which increase the amount of SO_4^{2-} in the surface of solid acid [18]. Solid acidity is strong to carbonize ionic liquid partially, and block acid sites on the surface of solid acid to reduce the material activity, so its desulfurization rate is lower than PSO. For Zr element, it can be determined that binding structure of SO_4^{2-} to Zr ions exhibits the bridged bidentate form [21]. As the SO_4^{2-} group existed, due to the strong attracting electrons from Zr ions via two covalent S=O bonds, the center of metal atom lacks electrons severely, thus strong Lewis acidic strength is generated (Fig. 2), which could adsorb benzothiophene easily. That's the reason why the desulfurization rate of PSO is higher than PSS.

Conclusions

In the present investigation, PSMIM and $PSMIMHSO_4$ were successfully prepared. Then two ionic liquids mixed with ZrO_2 at room temperature and compounded with ZrO_2 at 433 K which displayed solid acidity. The best reaction temperature was determined at 353 K with using $PSMIMHSO_4$ compounded with ZrO_2 at 433 K, whose the optimum mass ratio is 1:1. Through the comparison for the materials' activity of PSMIM, $PSMIMHSO_4$, ZrO_2, ZrO_2/SO_4^{2-}, $ZrOCl_2$, PSO, PSS and PSC, the desulfurization activity of PSO was higher than others under the same conditions. The desulfurization efficiency of PSO reached 97.4 %.

Acknowledgments Research was sponsored by The Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

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